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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Since the scientific work supported by the grants listed on the cover page of this report is continuing without a break either in its technical thrust or in its ARO sponsorship, the present report can be brief. It covers the progress achieved in this DNA-supported project over the four-and-a-half-year period from 1 July 1975 to 31 December 1979, a period during which its research has ranged over four areas: Evaluation of the atmospheric chemistry of neutral species; Kinetics of certain ion clustering reactions; Reactions of nitrogen metastables;

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and fluorescence lifetime studies of air triatomics, particularly NO_2^-. It should be pointed out that for a grant of very modest size (annual budgets in the \$30,000 to \$40,000 range), the work has been very productive, having resulted in ten publications (in four different journals and one book chapter). Its productivity continues to be high: One paper has recently been submitted for publication and another one is in preparation. The selection of subject matter is now undergoing moderate changes as it has done at various times in the past. The work on air metastables is being stepped up vigorously, that on fluorescence lifetime studies of triatomics is being phase out, and a new project on infrared chemiluminescence as a result of exothermic processes by excited species is being added.

In the main part of this report, the principal accomplishments are briefly and chronologically reviewed. Their detailed account may be found in the publications which are listed following this brief description.

CHEMICAL REACTIONS, RADIATIVE AND ENERGY TRANSFER PROCESSES OF IMPORTANT ATMOSPHERIC SPECIES.

Final Report.

Frederick Kaufman

23 April 1980

U. S. Army Research Office

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Department of Chemistry

University of Pittsburgh

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INTRODUCTION

Since the scientific work supported by the grants listed on the cover page of this report is continuing without a break either in its technical thrust or in its ARO sponsorship, the present report can be brief. It covers the progress achieved in this DNA-supported project over the four-and-a-half-year period from 1 July 1975 to 31 December 1979, a period during which its research has ranged over four areas: Evaluation of the atmospheric chemistry of neutral species; Kinetics of certain ion clustering reactions; Reactions of nitrogen metastables; and fluorescence lifetime studies of air triatomics, particularly NO_2. It should be pointed out that for a grant of very modest size (annual budgets in the $30,000 to $40,000 range), the work has been very productive, having resulted in ten publications (in four different journals and one book chapter). Its productivity continues to be high: One paper has recently been submitted for publication and another one is in preparation. The selection of subject matter is now undergoing moderate changes as it has done at various times in the past. The work on air metastables is being stepped up vigorously, that on fluorescence lifetime studies of triatomics is being phased out, and a new project on infrared chemiluminescence as a result of exothermic processes by excited species is being added.

In the main part of this report, the principal accomplishments are briefly and chronologically reviewed. Their detailed account may be found in the publications which are listed following this brief description.

PRINCIPAL ACCOMPLISHMENTS

It should be noted that this summary will confine itself to published papers and will therefore appear to be somewhat more disjointed and incomplete than the sum of the progress reports that were submitted during that period. However, in representing the total published output, the summary better describes the overall progress of the program.

In a paper entitled Hydrogen Chemistry: Perspective on Experiment and Theory, published as a chapter in Atmospheres of Earth and the Planets, B. M. McCormac (ed.), p. 219-232, 1975, the principal investigator reviewed the available arsenal of experimental techniques used to measure the rates of elementary reactions ranging from classical thermal and photochemical studies to flash photolysis and discharge-flow studies to state-to-state crossed molecular beam studies. Following a glimpse of reaction rate theory, the state of knowledge regarding seven important two-body and three-body reactions that involve OH and HO_2 was reviewed. It is ironic to note that in spite of continuing efforts, several of these critical steps are still poorly characterized. These include particularly the radical-radical reactions $OH + HO_2 \rightarrow H_2O + O_2$ and $H + HO_2 \rightarrow H_2 + O_2$, $OH + OH$, and $H_2O + O$.

In an attempt to measure the rate of the spin-forbidden reaction, $N(^4S) + CO_2 \rightarrow NO + CO$, the rate of formation of $O(^3P)$ was measured in the reaction of active nitrogen with CO_2. A paper by W. T. Rawlins and F. Kaufman, entitled the Reaction of CO_2 with Active Nitrogen, J. Chem. Phys., 64, 1128-1133 (1976), describes this work which was carried by resonance absorption at 130.2 nm in a discharge-flow apparatus at 298 K. The O-atoms were formed by the fast, secondary reaction of NO with excess $N(^4S)$ and their formation rate was measured under conditions of less than one percent conversion. This rate was found to be second-order in atomic nitrogen concentration, and the effective termolecular rate constant was found to vary inversely with the CO_2 concentration. These results were analyzed in terms of a mechanism in which CO_2 is dissociated by highly excited N_2 species, possibly $N_2(A^3\Sigma_u^+)$ in high vibrational states formed by N-atom recombination. It was also found that the direct two-body reaction has a rate constant less than 10^{-19} cm^3 s^{-1}, eight to nine orders of magnitude smaller than that of a fully allowed, exothermic atom-molecule reaction such as $N + NO \rightarrow N_2 + O$ or $O + NO_2 \rightarrow NO + O_2$.

A successful series of investigations in the field of ion-dipole cluster formation kinetics came to a close with a paper by V. M. Bierbaum, M. F. Golde, and F. Kaufman, entitled Flowing Afterglow Studies of Hydronium Ion Clustering Including Diffusion Effects, J. Chem. Phys., 65, 2715-2724 (1976). In it, the termolecular hydration sequence of H_3O^+ in He buffer gas,

$$H_3O^+(H_2O)_{n-1} + H_2O + He \rightleftarrows H_3O^+(H_2O)_n + He$$

was studied using the flowing afterglow technique. Forward rate constants for n = 1, 2, and 3, the reverse rate constant for n = 3, and the equilibrium constant for n = 4 was measured. The effects of mass discrimination, ion-electron dissociative recombination, and differing diffusion rates of the ions were considered, and the diffusion coefficients of the ions for n = 0 to 4 were estimated. The three forward rate constants were reported to be (6.65 ± 0.9), (15.1 ± 0.2), and (15 ± 4) x 10^{-28} cm^6 s^{-1} for n = 1, 2, and 3, respectively.

The first part of a series of papers dealing with the radiative and collisional properties of excited air triatomics, entitled Fluorescence Lifetime Studies of NO_2. I. Excitation of the Perturbed $^2B_2$ State Near 600 nm, by V. M. Donnelly and F. Kaufman, J. Chem. Phys., 66, 4100-4110 (1977) probed the nature of the fluorescence decays of NO_2 excited near 580 to 620 nm under collisionless conditions. Following excitation by a pulsed, frequency-narrowed dye laser, highly non-exponential decays were observed when strong absorption features were excited (e.g. at 585, 593, and 612 nm) whereas in weakly absorbing regions the decays were nearly exponential. This behavior could be explained in terms of the Bixon-Jortner model of state mixing of the excited $^2B_2$ state with vibrationally excited ground state $^2A_1$. This mixing, which distributes the oscillator strength of the $^2B_2 \rightarrow {}^2A_1$ transition among a large number of near-degenerate, perturbed upper states, is also responsible for the anomalously long lifetimes of these upper states whose character is principally that of vibrationally excited ground state. A partitioning of the total visible and near-u.v. absorption among the $^2B_2$ state and the somewhat higher lying $^2B_1$ state was also proposed. Based on spectroscopic data, quantum theoretical calculations, and calculated vibrational densities of states, the observed radiative lifetimes could be rationalized.

As part of our continuing program of line absorption or fluorescence measurements of atomic ground state and metastable species concentrations, we published a paper entitled Characteristics of O(I) and N(I) Resonance Line Broadening in Low Pressure Helium Discharge Lamps by W. T. Rawlins and F. Kaufman, J. Quant. Spectrosc. Radiat. Transfer, 18, 561-572 (1977). The resonance line broadening of O near 130 nm and of N near 120 nm was studied for a variety of r.f.- and microwave-excited low pressure He discharge lamps by measuring the fractional absorption of a given resonance line in the presence of known concentrations of absorbing ground-state O- or N-atoms in a flow cell at the entrance slit of a 0.5 m vacuum u.v. monochromator. For the O(I) lamps, non-thermal behavior was encountered, especially at low He pressure, suggesting that processes other than electron impact were involved in the excitation of the upperstate, e.g. O_2 + He (2^3S, 2^1S) → O* + O + He followed by emission of a 130 nm photon or radiative cascade to the emitting state. These processes could leave enough translational energy in the upper state to lead to a broadened line. Effective emitter temperatures up to 4300 K in r.f. lamps and up to 1100 K in microwave lamps were measured. These excitation transfer processes were found to be much less prevalent in N-atom lamps, probably because of the larger dissociation energy of N_2. Since resonance lamps of this type are finding increasing use in laboratory and field experiments involving excited "air" species, our successful analysis of emission characteristics has acquired added importance.

A preliminary communication entitled Mechanism of NO_2 Fluorescence Quenching, by V. M. Donnelly and F. Kaufman, J. Chem. Phys., 67, 4768-9 (1977) provided direct evidence for the stepwise vibrational deactivation mechanism of laser-excited NO_2. Fluorescence spectra were measured at NO_2 pressures from less than 0.1 mtorr to 10 mtorr or at 0.1 mtorr of NO_2 with increasing pressures of added He. Both the red shift of the fluorescence spectrum and the sharp decrease of the banded-to-continuum intensity ratio with increasing pressure supported the model of stepwise collisional deactivation in the perturbed, mixed $^2B_2$ state. The supposed pressure-independence of this banded-to-continuum fluorescence emission intensity ratio suggested as a result of earlier magnetic quenching experiments by Levy and coworkers, J. Chem. Phys., 62, 815 (1975), led to a published comment by Levy, J. Chem. Phys., 68, 5670 (1978), and reply by us, J. Chem. Phys., 68, 5671 (1978), in which we showed the magnetic quenching results to be clearly incompatible with other known properties of the low pressure fluorescence of NO_2.

The second major paper in this series, Fluorescence Lifetime Studies of NO_2. II. Dependence of the Perturbed $^2B_2$ State Lifetime on Excitation Energy, by V. M. Donnelly and F. Kaufman, J. Chem. Phys., 69, 1456-1460 (1978), expanded the laser excitation wavelength range to the blue and red, from 473 to 659 nm. Radiative lifetimes and quenching rates of the perturbed $^2B_2$ state were measured, and the dependence of the radiative lifetime on excitation energy was found to agree well with the calculated level density ratio of the $^2A_1$ and $^2B_2$ states. The fluorescence decays were seen to become more nearly exponential at higher excitation energy, the lifetime of the longer-lived (more statistically mixed) component of the fluorescence was found to decrease smoothly with increasing excitation energy, and the quenching rate constant was also found to decrease with increasing excitation energy. These trends were discussed and explained in terms of the general model leading to the resolution of the lifetime anomaly in NO_2.

The third part of the series, Fluorescence Lifetime Studies of NO_2. III. Mechanism of Fluorescence Quenching, by V. M. Donnelly, D. G. Keil, and F. Kaufman, J. Chem. Phys., 71, 659-673 (1979), addressed itself to the quenching of spectrally resolved features of the fluorescence as function of pressure, quencher species, and fluorescent wavelength, i.e. banded structure or continuum. Two distinct collisional processes were identified, a fast (gas kinetic to super gas kinetic) induced internal energy transfer process that removes little energy from the excited NO_2 molecule; and a slower (~0.1 gas kinetic) stepwise vibrational energy transfer process that removes about 1000 cm^{-1} per collision. The former process is associated with the quenching of the banded structure and the latter with that of the continuum. Both processes were measured at 298 K for 12 added gases: two monatomic (He, Ar), four diatomic (H_2, D_2, O_2, N_2), and six polyatomic (CO_2, H_2O, D_2O, NH_3, ND_3, SF_6). The rate constants for the fast process ranged from 0.38 to 2.0 times gas kinetic and those of the slow process from 0.04 to 0.52 times gas kinetic. The entire range and mechanism of collisional quenching processes was thus clarified and found to be consistent with all available data.

A brief, preliminary study of the reactions of $N(^2D, ^2P, \text{and } ^4S)$ with Cl_2 was described in a communication entitled Flow Tube Measurement of the Rate Constants of the $N(^2D, ^2P, \text{and } ^4S) + Cl_2$ Reactions, by M. P. Iannuzzi and F. Kaufman, J. Am. Chem. Soc., 101, 4002-3 (1979). With the use of resonance fluorescence detection of $N(^2D)$ at 149.2 and of $N(^2P)$ at 174.2 nm, detection limits of (1-2) x 10^9 cm^{-3} could be achieved. For the much slower $N(^4S)$ reaction, the intensity of the (11, 7) band of the ($B^3\pi \rightarrow A^3\Sigma_u^+$) transition of N_2 was used to monitor [N]. Rate constants of 3.6 x 10^{-11}, 2.2 x 10^{-11}, and ~2 x 10^{-15} cm^3 s^{-1} were measured for the three species in the above order. This study has shown the specificity and versatility of the flow tube technique, not only in the measurement of elementary reaction steps under such conditions that side reactions cannot interfere, but also in the probing of reaction channels through accurate monitoring of product species such as $Cl(^2P_{3/2,\ 1/2})$.

In conclusion, recently completed work as well as continuing and planned phases of our research effort should be mentioned: The fourth and final paper in our series on NO_2 fluorescence has been submitted to J. Chem Phys., an experimental study of the $N(^2D$ or $^2P) + O_2$ reactions and of the $N(^2D) + O$ reaction has been completed and is being written up for publication, and new work on the kinetics of $N_2(A^3\Sigma_u^+)$ reactions is well on its way.

LIST OF PUBLICATIONS ARISING FROM ABOVE ARO GRANTS

1. Hydrogen Chemistry: Perspective on Experiment and Theory, F. Kaufman, in Atmospheres of the Earth and the Planets, B. M. McCormac (ed.), D. Reidel Publishing Co., Dordrecht, Holland, p. 219 (1975).

2. The Reaction of CO_2 with Active Nitrogen, W. T. Rawlins and F. Kaufman, J. Chem. Phys., 64, 1128 (1976).

3. Flowing Afterglow Studies of Hydronium Ion Clustering Including Diffusion Effects, V. M. Bierbaum, M. F. Gold, and F. Kaufman, J. Chem. Phys., 65, 2715 (1976).

4. Fluorescence Lifetime Studies of NO_2. I. Excitation of the Perturbed $^2B_2$ State Near 600 nm, V. M. Donnelly and F. Kaufman, J. Chem. Phys., 66, 4100 (1977).

5. Characteristics of OI and NI Resonance Line Broadening in Low Pressure Helium Discharge Lamps, W. T. Rawlins and F. Kaurman, J. Quant. Spectrosc. and Radiad. Transf., 18, 561 (1977).

6. Mechanism of NO_2 Fluorescence Quenching, V. M. Donnelly and F. Kaufman, J. Chem. Phys., 67, 47[illegible] (1977).

7. Fluorescence Lifetime Studies of NO_2. II. Dependence of the Perturbed $^2B_2$ State Lifetimes on Excitation Energy, V. M. Donnelly and F. Kaufman, J. Chem. Phys., 69, 1456 (1978).

8. Reply to Comment on "Mechanism of NO_2 Fluorescence Quenching," V. M. Donnelly and F. Kaufman , J. Chem. Phys., 68, 5671, 1978.

9. Fluorescence Lifetime Studies of NO_2. III. Mechanism of Fluorescence Quenching, V. M. Donnelly, D. G. Keil, and F. Kaufman, J. Chem. Phys., 71, 659 (1979).

10. Flow Tube Measurement of the Rate Constants of the N(^2D, ^2P, and ^4S) + Cl_2 Reactions, M. P. Iannuzzi and F. Kaufman, J. Amer. Chem. Soc., 101, 4002 (1979).